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Part I

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RESEARCH ON SYNTHESIS PROCEDURES FOR INTERMEDIATES  
REQUIRED FOR HIGH TEMPERATURE STABLE  
POLYMERIC MATERIALS

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TECHNICAL REPORT AFML-TR-69-326, Part I

December 1969

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## FOREWORD

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under USAF Contract No. F33615-69-C-1351, "Research on Synthesis Procedures for Intermediates Required for High Temperature Stable Polymeric Materials." The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. George Moore (MANP), as Project Scientist.

This technical report covers the work conducted from 15 December 1968 to 15 October 1969. The manuscript was released by the authors in November 1969 for publication as a technical report.

The work was carried out by Messrs. K. R. Fountain, R. N. Clark, and L. W. Breed, Dr. Fountain acted as principal investigator for Midwest Research Institute during most of the report period; Mr. Breed prepared this report. The authors are indebted to Mr. C. E. Bricker and Miss M. E. Whitehead for their contributions to the research.

This technical report has been reviewed and is approved.



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## ABSTRACT

Work on the synthesis of the following substances is reported: ruthenocene, 1,1'-diiodoferrocene, triphenylsilicon azide, 1,1'-dibromoferrocene, 1-iodo-2,3,5,6-tetrafluorobenzene, 1,4-diiodo-2,3,5,6-tetrafluorobenzene, 4,5-dinitro-N,N-o-phenylenebis(p-toluenesulfonamide), poly[(7-oxo-7H,10H-benz[de]imidazo-[4',5':5,6]benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL), benzidine 3,3'-dicarboxylic acid, diethyl 2,5-diaminoterephthalate, and 6,6'-bis([4H],3,1-benzoxazine-2,4-[1H] dione).

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## I.

### INTRODUCTION

It is the purpose of this research to prepare various classes of compounds for use as intermediates in the synthesis of high temperature stable polymeric materials. The methods to be used are either improved established procedures or newly devised, unique procedures.

During this report period, work has been carried out on the preparation of the following substances: (1) Ruthenocene, (2) 1,1'-diiodoferrocene, (3) triphenylsilicon azide, (4) 1,1'-dibromoferrocene, (5) 1-iodo-2,3,5,6-tetrafluorobenzene, (6) 1,4-diiodo-2,3,5,6-tetrafluorobenzene, (7) 4,5-dinitro-N,N-o-phenylenebis(p-toluenesulfonamide), (8) poly[(7-oxo-7H,10H-benz[de]imidazo-[4',5':5,6]benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl](BBL), (9) benzidine 3,3'-dicarboxylic acid, (10) diethyl 2,5-diaminoterephthalate, and (11) 6,6'-bis([4H], 3,1-benzoxazine-2,4-[1H]dione). Specified samples of (3), (4), (5), (6), (7), and (8) have been prepared and submitted to the Materials Laboratory. Smaller samples of (1), (2), and (10) were submitted. Additional (1) was supplied through purchase and further work on (2) was discontinued. Work is continuing on (9), (10), and (11).

## II.

### RESULTS AND DISCUSSION

#### A. Ruthenocene

This compound was prepared by a procedure supplied by the Materials Laboratory (Ref. 1) in several small scale experiments, then a 2-lb. sample was purchased, analyzed, and forwarded to the Materials Laboratory.

1. Synthesis: In three experiments at the 0.024, 0.042, and 0.097 molar levels, the yields of ruthenocene ranged from 19-27%. A total of 5.5 g. of purified ruthenocene was obtained and shipped to the Materials Laboratory.

2. Physical properties: The 5.5-g. sample, which had been recrystallized from methanol, melted at 201-202°.\* Its infrared spectrum is reported in Figure 1.\*\* The 2-lb. sample melted at 200-201°. Its infrared spectrum is reported in Figure 2.

3. Purity: G.l.c. analysis of the 5.5-g. sample (1-m. column, 5% SE 30 on Chromoport XXX, N carrier, 60 ml/min, 107°) indicated 99% purity. G.l.c. analysis of the 2-lb. sample (Figure 3) (1-m. column, 5% SE 30 on Chromoport XXX, N carrier, 60 ml/min, 117°) was 98% pure. Three samples of the 2-lb. quantity were submitted for elemental analyses.

Anal. Calcd. for  $C_{10}H_{10}Ru$ : C, 51.92; H, 4.37. Found: C, 52.33, 51.96, 50.84; H, 4.32, 4.46, 4.37.

Determination of metal content by emission spectrophotometry indicated 99.6-99.8% ruthenium by difference.

#### B. 1,1'-Diiodoferrocene

A proprietary procedure provided by the Materials Laboratory was followed in the synthesis of this compound (Ref. 1).

1. Synthesis: After a series of preparations ranging in size from 0.03 molar to 0.46 molar in which yields of 19-35% of diiodoferrocene were obtained, a 25-g. sample was purified and forwarded to the Materials Laboratory.

\* All temperatures are reported in °C.

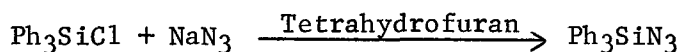
\*\* All figures are found at the end of the report, p. 16.

2. Physical properties: Infrared peaks were observed at 1395, 1375, 1339, 1140, 1018, 867, and 822  $\text{cm}^{-1}$ .

3. Purity: By g.l.c., the 25-g. sample was found to be 99.1% pure (1-m. column, 5% SF-96 on Gas Chrom Q).

### C. Triphenylsilicon Azide

This substance was prepared by a method described by Thayer and West (Ref. 2).



Triphenylsilicon chloride was purified by heating it with thionyl chloride for four days, distilling off the excess thionyl chloride, and recrystallizing the triphenylsilicon chloride. The tetrahydrofuran was dried over molecular sieves before use.

1. Synthesis: In a typical procedure, 53.5 g. (0.40 mole) of aluminum chloride and 135 g. (2.08 moles) of sodium azide in 2 liters of tetrahydrofuran were stirred and refluxed for 1.5 hr., and then 179.0 g. (0.61 mole) of chlorotriphenylsilane was added. After heating was continued for an additional 48 hr., no g.l.c. peak for chlorotriphenylsilane could be detected in the mixture. When the mixture was filtered and the tetrahydrofuran removed on a rotary evaporator, a yellow solid was obtained, which was recrystallized from petroleum ether, b.p. 60-90°, to obtain 120 g. (66%) of triphenylsilicon azide, m.p. 82-83°. A second recrystallization in which a portion of the product was lost gave 54 g., m.p. 82-83°, another 50-g. batch of triphenylsilicon azide, m.p. 82-83°, was obtained in a repetition of the experiment on a smaller scale.

2. Physical properties: The substance melted at 82-83°. Infrared spectra of the two portions of the sample that was forwarded to the Materials Laboratory are reproduced in Figures 4 and 5.

3. Purity: Purity of the triphenylsilicon azide was assessed in terms of its elemental analysis.

Anal. Calcd. for  $\text{C}_{18}\text{H}_{15}\text{SiN}_3$ : C, 71.72; H, 5.02; N, 13.94. Found: (No. 1) C, 71.68; H, 5.03; N, 13.80; (No. 2) C, 72.03; H, 5.07; N, 13.81.

#### D. 1,1'-Dibromoferrocene

This compound was prepared by a procedure supplied by the Materials Laboratory (Ref. 1).

1. Synthesis: The necessary replications of the experimental procedure afforded a series of samples of 1,1'-dibromoferrocene that were forwarded to the Materials Laboratory as specified in Table I. In addition, a total of 58.2 g. of unpurified 1,6'-dibromobiferrocenyl, which was obtained as a by-product in the synthesis, was also forwarded to the Materials Laboratory.

TABLE I

#### SUMMARY OF 1,1'-DIBROMOFERROCENE SAMPLES

<u>Sample No.</u>	<u>Weight (g.)</u>	<u>M.P. (°C)</u>	<u>Purity (%)<sup>a/</sup></u>
1	27.2	53-54	95.2
2	52.1	53-54	94.7
3	24.0	53-54	92.4
4	131.5	52-54	97.5
5	175.4	-	97.6
6	95.0	52-53	98.6
7	37.6	51-52	97.8
8	100.0	51-52	94.2
9	32.4	50-52	93.3
10	113.9	39-42	63.7

<sup>a/</sup> Gas-liquid chromatography (g.l.c) analyses were carried out on either one of the two following columns: 1-m. 5% SF 96 on Gas Chrom Q, N<sub>2</sub> carrier, 60 ml/min, 150°; 2-m. 5% SF 96 on Gas Chrom Q, He carrier, 50 ml/min, 165°. Purity determinations ( $\pm$  1%) are based on cutting and weighing areas of Xerox copies of the chromatograms.

2. Physical properties: 1,1'-Dibromoferrocene was an orange crystalline solid that could be sublimed. Melting points of samples with various purities are summarized in Table I and a typical infrared spectrum is reported in Figure 6.

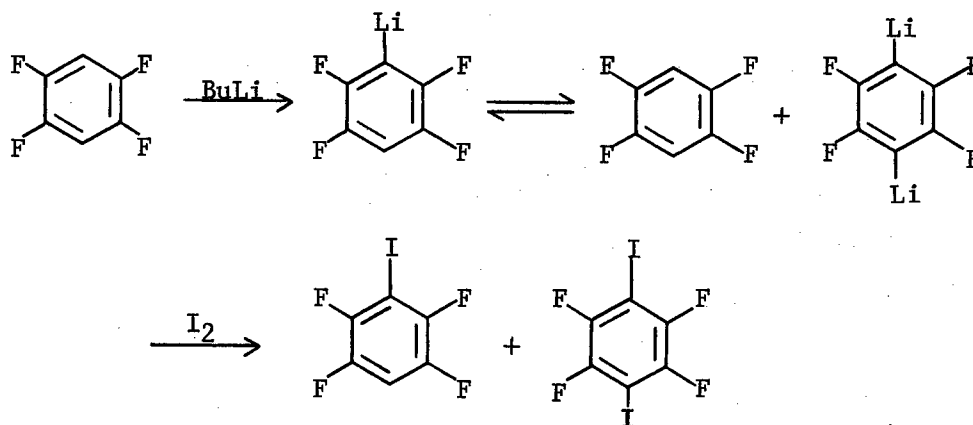
3. Purity: Purities of the samples determined by g.l.c. are also summarized in Table I. A total of 439.5 g. had a purity of 97% or better, an additional 235.7 g. had a purity better than 92%, and 113.9 g. was 64%

pure. A typical g.l.c. analysis is reported in Figure 7. The following is a microanalysis for a sample with a 93% g.l.c. purity.

Anal. Calcd. for  $C_{10}H_{10}FeBr_2$ : C, 34.92; H, 2.35. Found: C, 35.15; H, 2.28.

E. 1-Iodo-2,3,5,6-tetrafluorobenzene and 1,4-Diiodo-2,3,5,6-tetrafluorobenzene

These compounds were prepared by the following procedure, which was provided by the Materials Laboratory (Ref. 1).



The samples forwarded to the Materials Laboratory are summarized in Table II.

1. Synthesis: In a typical experiment a solution of 100 g. (0.67 mole) of 2,3,5,6-tetrafluorobenzene in 1,400 ml. of tetrahydrofuran, which has been dried over  $LiAlH_4$ , was cooled to  $-60$  to  $-70^\circ$  in an acetone-Dry Ice bath and treated slowly with 420 ml. (0.67 mole) of 1.6 molar *n*-butyllithium in hexane. After the mixture was stirred 30 min., 170 g. (0.67 mole) of iodine was added through a solids addition funnel, and stirring was continued for an additional 30 min. at  $-60^\circ$ . The added iodine remained unchanged. The cooling bath was removed and the stirred mixture was allowed to warm to room temperature. At  $-35^\circ$  condensation with the solid iodine began and at  $-10^\circ$  all the iodine had dissolved. After the mixture was stirred at room temperature over a weekend, it was hydrolyzed with 100 ml. of 10% hydrochloric acid, the organic phase was separated, and the aqueous phase was washed with three 200-ml. portions of ether. The combined organic phases were washed with aqueous sodium bisulfite and evaporated on a rotary evaporator to obtain 207 g. of crude product, which by g.l.c. analysis contained 69% of 1-iodo-2,3,5,6-tetrafluorobenzene and 31% of 1,4-diiodo-2,3,5,6-tetrafluorobenzene. When the product from this experiment was combined with

TABLE II

SUMMARY OF 1-iodo-2,3,5,6-tetrafluorobenzene AND  
1,4-diiodo-2,3,5,6-tetrafluorobenzene SAMPLES

<u>Sample No.</u>	<u>Weight (g.)</u>	<u>M.P. (°C) or B.P. [°C (mm.)]</u>	<u>G.L.C. Purity (%)</u>
1-Iodo-2,3,5,6-tetrafluorobenzene			
1	39.6	-	100 <sup>a</sup> /
2	43.5	39 (2)	97 <sup>b</sup> /
3	41.4	43 (2)	97 <sup>b</sup> /
4	35.7	39 (2)	96 <sup>b</sup> /
5	116.0	39 (2)	97 <sup>b</sup> /
1,4-Diiodo-2,3,5,6-tetrafluorobenzene			
6	27.1	-	100 <sup>a</sup> /
7	29.5	110-111	95 <sup>c</sup> /
8	106.5	111-112	98 <sup>c</sup> /
9	71.5	110-111	95 <sup>c</sup> /
10	14.7	110-112	98 <sup>c</sup> /
11	3.0	111-112	94 <sup>c</sup> /
12	9.0	110-112	92 <sup>c</sup> /

a/ 2-m. column, 5% SF 96 on Gas Chrom Q, He carrier, 65 ml/min, 110°.

b/ 2-m. column, 20% SF 96 on Gas Chrom Q, He carrier, 45 ml/min, 125°.

c/ 2-m. column, 20% SF 96 on Gas Chrom Q, He carrier, 40 ml/min, 181°.

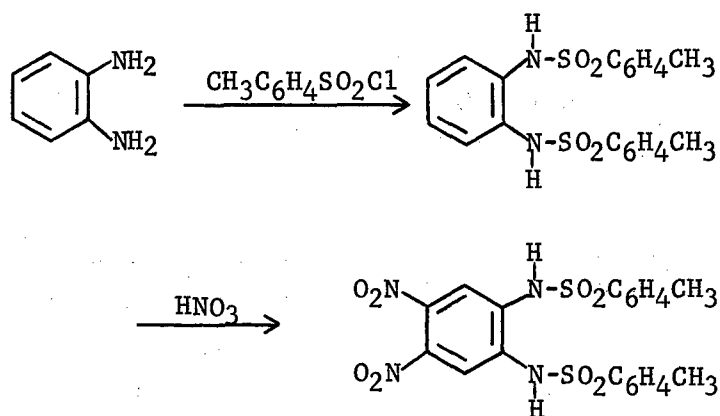
the products from four similar experiments and distilled through a 40 cm. Vigreux column, 243 g. (18%) of 1-iodo-2,3,5,6-tetrafluorobenzene was obtained. One recrystallization of the combined residues from *n*-heptane gave 257 g. (19%) of a series of crops of 1,4-diiodo-2,3,5,6-tetrafluorobenzene. Redistillation or recrystallization with charcoal of these products gave the samples 2 to 5 and 7 to 12 summarized in Table II.

2. Physical properties: The boiling point of 1-iodo-2,3,5,6-tetrafluorobenzene was 39° (2 mm.) and its melting point (sample 5) was -17 to -14°. The infrared spectrum of sample 5 is reported in Figure 8. Purest samples of 1,4-diiodo-2,3,5,6-tetrafluorobenzene melted at 111-112°. The infrared spectrum of sample 8 is reported in Figure 9.

3. Purity: Purity of the samples was assessed in terms of g.l.c. analysis and the results are reported in Table II. The g.l.c. conditions used for samples 1 and 6 were not satisfactory to separate the impurities and the g.l.c. purity recorded probably does not reflect the actual purity. G.l.c. traces for samples 5 and 8 are reported in Figures 10 and 11, respectively.

F. 4,5-Dinitro-N,N'-o-phenylenebis(p-toluenesulfonamide)

A pilot experiment has been completed on the preparation of this compound by a method supplied by the Materials Laboratory (Ref. 1).



Since starting materials were inexpensive and the manipulations not difficult, the pilot experiment was carried out on a 1 mole scale. A 235-g. sample from this experiment was forwarded to the Materials Laboratory.

1. Synthesis: A stirred mixture of 750 ml. of pyridine and 114 g. (1.05 moles) of o-phenylenediamine, m.p. 99-100°, which had been purified by recrystallization from water with sodium hydrosulfite and charcoal, was treated with 404 g. (2.12 moles) of p-toluenesulfonylchloride in 300 ml. of pyridine at a rate that maintained the temperature at 60°. After the mixture was stirred overnight at 60°, the cooled product was added to 9.0 liters of 15% hydrochloric acid. When the precipitated material was filtered off and recrystallized from 3.0 liters of acetic acid, 308 g. (71%) of N,N'-o-phenylenebis(p-toluenesulfonamide), m.p. 202-204° was obtained (reported m.p. 203°) (Ref. 5).

A slurry of 307 g. (0.74 mole) of N,N'-o-phenylenebis(p-toluenesulfonamide) in 3.5 liters of glacial acetic acid was heated to 60° and treated with one-third of a nitrating mixture prepared from 100 ml. of fuming nitric acid and 117 ml. of glacial acetic acid. The reaction was



not exothermic. After being stored over a weekend, the mixture was reheated to 65°, and after 1.5 hr., the remainder of the nitrating mixture was added slowly, the temperature increasing to 70° and being maintained at that temperature by the rate of addition. After the addition was complete, heating was continued for 1 hr. After the precipitated product was filtered off and recrystallized from glacial acetic acid, and dried at 80-100° in a vacuum oven for 3 hr., 236 g. (63%) of 4,5-dinitro-N,N'-o-phenylenebis(p-toluenesulfonamide) was obtained.

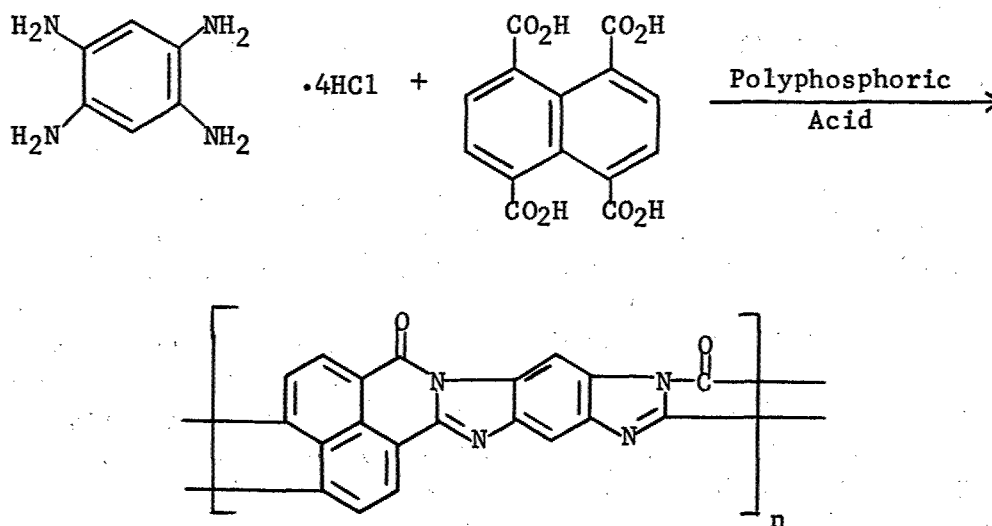
2. Physical properties: 4,5-Dinitro-N,N'-o-phenylenebis(p-toluenesulfonamide) melted at 243-245 (dec.) [reported m.p., 248-250° (dec.)] (Ref. 6). Its infrared spectrum is reported in Figure 13.

3. Purity: No impurities were evident in the sample according to elemental analyses.

Anal. Calcd. for  $C_{20}H_{18}N_4S_2O_8$ : C, 47.43; H, 3.58; N, 11.06; S, 12.66. Found: C, 47.49; H, 3.77; N, 11.11; S, 12.46.

G. Poly[(7-oxo-7H,10H-benz[de]imidazo-[4',5':5,6]benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL)

The polymer was prepared by a method supplied by the Materials Laboratory (Ref. 1) which is similar to a method described in the literature (Ref. 4).



A 12-g. sample has been prepared and forwarded to the Materials Laboratory.

1. Synthesis: When 50 g. of the amine hydrochloride in 400 ml. of deoxygenated water was treated under nitrogen with 8 g. of charcoal, filtered, and the filtrate was treated with 400 ml. of concentrated hydrochloric acid, 1,2,4,5-tetraaminobenzene tetrahydrochloride precipitated. After the precipitated hydrochloride was filtered off and washed with tetrahydrofuran and ether, it was dried under vacuum oven at 80° over P<sub>2</sub>O<sub>5</sub>, then stored over P<sub>2</sub>O<sub>5</sub> in a desiccator under vacuum. The 39.8 g. of 1,2,4,5-tetraaminobenzene tetrahydrochloride was obtained.

Anal. Calcd. for C<sub>6</sub>H<sub>14</sub>Cl<sub>4</sub>N<sub>4</sub>: C, 25.36; H, 4.97; N, 19.72. Found: C, 25.86; H, 5.04; N, 19.35.

Since considerable time elapsed before the polymer was prepared, the 39.8-g. sample was again reprecipitated to obtain 35.6 g. of tetraaminobenzene tetrahydrochloride, which was a pale lavender solid after it was dried over phosphorus pentoxide at 80° (0.05 mm.). The infrared spectrum is reported in Figure 13.

Anal. Found: C, 26.12; H, 5.70; N, 15.25.

Naphthalene tetracarboxylic acid was reprecipitated twice by the following procedure: A 16.2 g.-sample (0.053 mole) of naphthalene tetracarboxylic acid, which had been received from the Materials Laboratory, was dissolved by heating it for 15 min. at 60-70° in 75 ml. of an aqueous solution containing 13.8 g. (0.21 mole) of potassium hydroxide. After the pH was adjusted to 7 with dilute hydrochloric acid, the tetra-substituted potassium salt was precipitated with 250 ml. of cold methanol. The salt was redissolved in 200 ml. of cold water and reprecipitated with 50 ml. of 10% hydrochloric acid. After the acid was centrifuged off and washed three times with distilled water, it was dried overnight over sulfuric acid at 25° (0.1 mm.). The infrared spectrum (Figure 14) still showed a minor peak at 1770 cm<sup>-1</sup>, which could be attributed to a minor portion of anhydride. The spectrum of the BBL polymer that was provided by the Materials Laboratory also shows a weak band in this region.

Anal. Calcd. for C<sub>14</sub>H<sub>8</sub>O<sub>8</sub>: C, 55.28; H, 2.65. Found: C, 53.23; H, 3.42.

After nitrogen was passed through 800 ml. of polyphosphoric acid overnight and the solvent was cooled to room temperature, 11.3192 g. (0.03985 mole) of 1,2,4,5-tetraaminobenzene tetrahydrochloride was added and the mixture was reheated and stirred at 75° overnight, after which hydrogen chloride was no longer evolved. The cooled solution was treated with 12.1230 g. (0.02985 mole) of 1,4,5,8-naphthalene tetracarboxylic acid, heated slowly to 180°, and then heated at 180° for 19 hr. A portion of solid material that formed on the surface was broken loose and allowed to redissolve during this

heating period. At the end of the heating period, the hot solution was poured out, cooled, and washed free of acid with methanol in small portions in a Waring Blendor. After the polymer was dried at 200° (0.3 mm.) for 4 hr., 13.6 g. (calcd. 13.3 g.) of a black solid was obtained, which dissolved after 18 hr's stirring in 2 kg. of methanesulfonic acid and filtered. The filtrate was added slowly to 8 liters of stirred methanol, and the precipitated polymer was filtered off. Six successive washings with 2 liters of methanol removed the residual acid. There was obtained 12.1 g. (91%) of the BBL polymer. Some loss was incurred during the filtration.

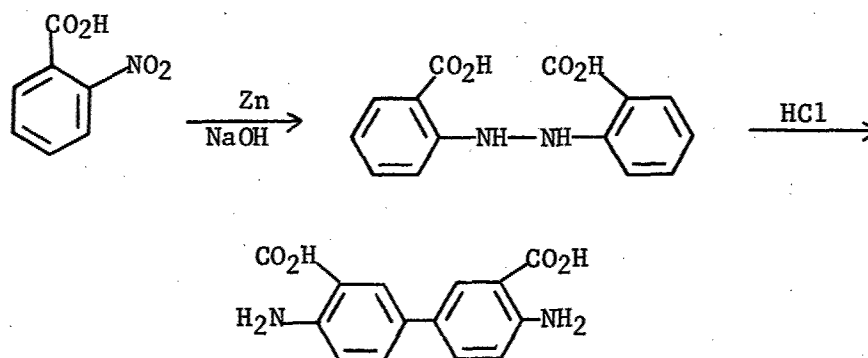
2. Physical properties: The following inherent viscosities were obtained at the specified concentrations (methanesulfonic acid at 30°): 0.5%, 2.31 dl/g; 0.25%, 2.55 dl/g; and 0.125%, 2.86 dl/g. An infrared spectrum of the polymer is reproduced in Figure 15.

3. Purity: An elemental analysis of the polymer was obtained.

Anal. Calcd. for  $C_{20}H_6N_4O_2$ : C, 71.86; H, 1.81; N, 16.76. Found: C, 68.00; H, 2.63; N, 15.88; ash, 0.003%.

#### H. Benzidine 3,3'-Dicarboxylic Acid

After an attempt to purify commercially available material from Pfaltz and Bauer, Inc., failed, the preparation of this substance followed the method reported by Fierz-David and Blangley (Ref. 5).



Preliminary experiments validated the procedure, and subsequently two larger scale experiments afforded 719 g. of material that has not yet been fully purified. The following is an example of the method of synthesis. After 500 g. (3.00 moles) of *o*-nitrobenzoic acid was dissolved in a solution of 950 ml. of water containing 500 g. of sodium hydroxide, zinc dust was added incrementally until the mixture became pale yellow (less than

750 g., 11.5 g.-atoms were required). The resulting solution, diluted with 4 liters of hot water was filtered to remove the unchanged zinc. The filtrate was treated with 300 ml. of 2N acetic acid, a small amount of  $\text{NaHSO}_3$ , and sufficient concentrated hydrochloric acid (about 1,700 ml.) to adjust the pH to 4. The crude hydrazobenzoic acid was filtered off and treated with 840 ml. of water and 640 ml. of concentrated hydrochloric acid and then heated at 90-100° for 18 hr. The product was filtered hot and the insoluble residue was washed with 115 ml. of concentrated hydrochloric acid and 200 ml. of water. The combined filtrate and washings were warmed to 70-80° and treated with concentrated ammonium hydroxide until a pH of 4 was obtained and then with 225 g. of sodium acetate in 525 ml. of water. The precipitated 3,3'-benzidine dicarboxylic acid was collected by filtration and dried under vacuum at 80-90°. The material was partly purified by precipitating it from solution in 10% hydrochloric acid with saturated sodium bicarbonate. A total of 331 g. (81%) of benzidine 3,3'-dicarboxylic acid was obtained. A portion of this material that precipitated at pH 4 and melted at 194-201° (differential thermal analysis) had the following elemental analysis.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$ : C, 61.76; H, 4.44; N, 10.29. Found: C, 63.15, 63.40; H, 5.08, 5.04; N, 12.19, 11.70.

Purification of 388 g. of the impure benzidine 3,3'-dicarboxylic acid was carried out in two batches. In one experiment 194 g., ground in a mortar, dissolved in 2 liters of 10% hydrochloric acid, and treated with saturated sodium bicarbonate until a pH of 4.5 was obtained. The precipitate was filtered off, washed with 1 liter of cold water, and dried at 120° (0.2 mm.) overnight to obtain 150 g. (74% recovery) of benzidine 3,3'-dicarboxylic acid. The product melted at 246-262° (differential thermal analysis). The infrared spectrum is reported in Figure 16. The product was forwarded to two analytical laboratories.

Anal. Calcd. for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$ : C, 61.76; H, 4.44; N, 10.29. Found (first analyst): C, 37.30; H, 3.37; N, 8.31; (second analyst) C, 56.10; H, 4.00; Cl, 13.96; ash, 19.11.

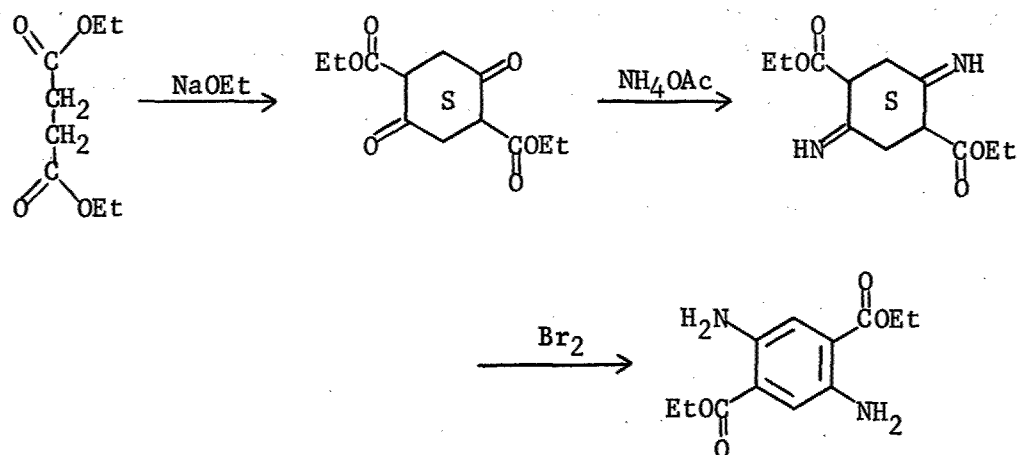
The remaining 202 g. of benzidine 3,3'-dicarboxylic acid was similarly precipitated from 1 liter of 10% hydrochloric acid. The recovered benzidine 3,3'-dicarboxylic acid (146 g., 73%) melted at 259-271° (differential thermal analysis). Its infrared spectrum is reported in Figure 17.

Anal. Found: (second analyst) C, 61.85; H, 4.45; Cl, 2.18; N, 10.45; ash, 3.36; (third analyst) C, 58.34; H, 4.35; Cl, 0.13; N, 10.20; ash, 2.72.

Additional washing with water will be required for the purification of these samples.

## I. Diethyl 2,5-Diaminoterephthalate

Pilot experiments are being carried out on the synthesis of this compound by a procedure supplied by the Materials Laboratory (Ref. 1).



A 7-g. sample of the product of the preliminary experiment was forwarded to the Materials Laboratory. With the concurrence of the Materials Laboratory, it was decided that an alternate procedure would be used in the large scale preparations (Ref. 6).

1. Synthesis: Sodium ethoxide was prepared by treating 55 g. (2.18 g.-atoms) of sodium with 650 ml. of dry ethanol and distilling off the excess alcohol under nitrogen. After 1 liter of dioxane and 163 g. (0.93 mole) of diethyl succinate were added sequentially with stirring, stirring was continued overnight at room temperature, and then the mixture was heated at  $50-55^\circ$  for 5 hr., and finally refluxed overnight. The mixture became so thick that an additional 200 ml. of dioxane was added. The resulting sodium salt was filtered and added to 2 liters of ice. After the mixture was neutralized with 10% acetic acid, the crude ester was filtered off. Recrystallization from 95% ethanol gave two crops of succinoylsuccinic acid diethyl ester, one, 72.7 g., with a m.p. of  $124-125^\circ$  and the other, 8.0 g., with a m.p. of  $119-121^\circ$ . The total yield was 67% [reported m.p.,  $126-127^\circ$  (Ref. 1)].

A mixture of 40 g. (0.16 mole) of succinoylsuccinic acid diethyl ester and 320 g. (4.1 moles) of ammonium acetate was heated in an oil bath for 5 hr. Although the oil bath was maintained at  $155-160^\circ$ , the temperature of the mass was  $125-130^\circ$ . During the heating period, ammonia and water were swept out with nitrogen. After the product was poured into 3 liters of ice water and the precipitated material was filtered off, a series of recrystallizations of the material from two preparations gave 22 g. (28%)

of succinoylsuccinic acid diethyl ester diimine, m.p. 174-177° [reported m.p., 177-180° (Ref. 1)].

After a solution of 18 g. (0.071 mole) of the diimine in 115 ml. of concentrated sulfuric acid was stirred at 40° and treated with 47 g. (0.25 mole) [in error this quantity was used rather than 18 g. (0.11 mole)] of bromine, the mixture was heated at 50° for 3.5 hr. and then purged with nitrogen overnight to remove the excess bromine. The mixture, poured into 750 ml. of ice water containing 1 g. of sodium sulfate, gave the pale yellow sulfate salt, which was filtered off and added directly to a solution of 193 g. of sodium acetate trihydrate in 400 ml. of water that was stirred during the addition. When the precipitate was filtered off, washed with water, dried, and recrystallized from methanol (charcoal used for decolorization), 7.6 g. (43%) of diethyl 2,5-diaminoterephthalate was obtained.

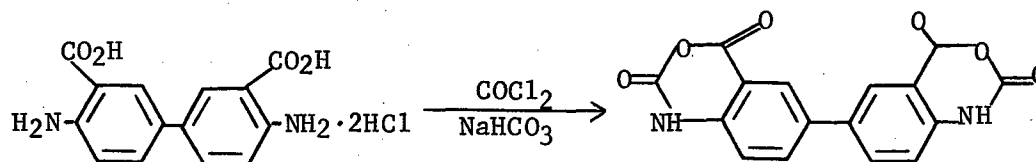
2. Physical properties: Diethyl 2,5-diaminoterephthalate was a bright pumpkin-colored solid that melted at 170-171°. Its infrared spectrum is reported in Figure 18.

3. Purity: The purity of the 7-g. sample was assessed in terms of its elemental analysis.

Anal. Calcd. for  $C_{12}H_{16}N_2O_4$ : C, 57.13; H, 6.38; N, 11.10. Found: C, 57.25; H, 6.47; N, 11.34.

J. 6,6'-Bis([ $4H$ ],3,1-benzoxazine-2,4-[ $1H$ ] dione)

This substance will be prepared by a method provided by the Materials Laboratory (Ref. 1) which is similar to a procedure that has been reported for the conversion of anthranilic acid to isotoic anhydride (Ref. 7), but employs a basic medium.



1. Synthesis: In a small scale experiment, a solution of 6 g. of unpurified benzidine 3,3'-dicarboxylic acid in 1 liter of water and 55 g. of sodium bicarbonate was boiled, treated with charcoal, and filtered to obtain a yellow solution through which phosgene was bubbled for 2.5 hr. at 10°. The precipitated solids were filtered off, washed with water, methanol, and light petroleum ether. The weight of the dried product was 2.1 g. No precipitation occurred when the 2.1 g. was dissolved in 150 ml. of dimethylacetamide, filtered, and cooled in a Dry Ice bath. Addition of 2.5 liters of methanol precipitated 0.8 g. of 6,6'-bis([4H],3,1-benzoxazine-2,4-[1H]-dione). Larger scale preparations are now under way.

2. Physical properties: The bisdione did not melt up to 500° (differential thermal analysis). Its infrared spectrum is reported in Figure 19.

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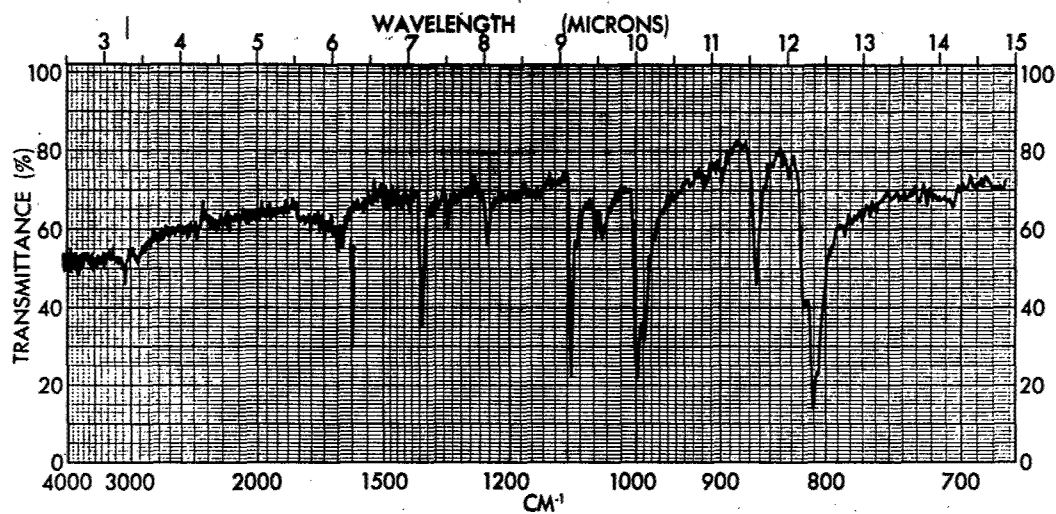


Figure 1 - Infrared Spectrum of Ruthenocene (5.5-g. sample)  
(KBr)

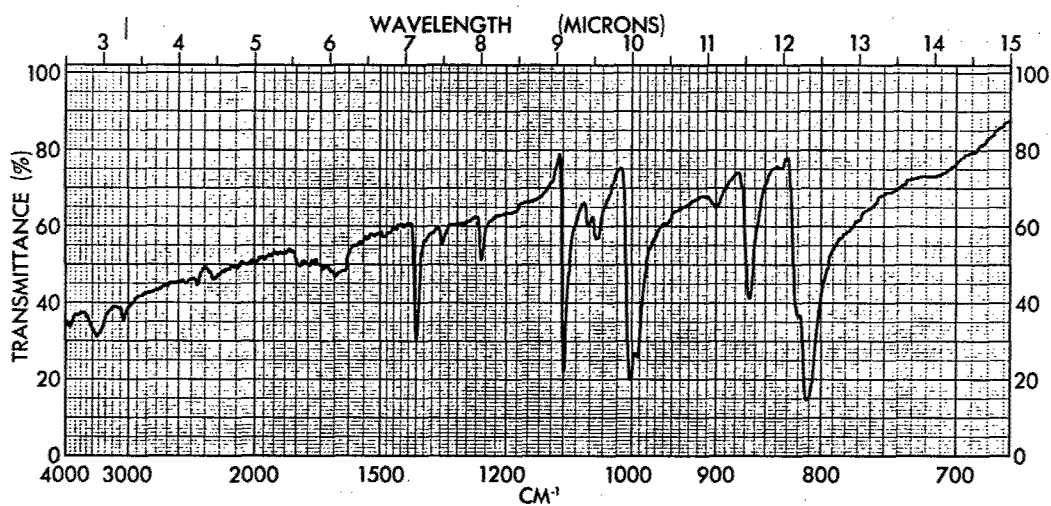


Figure 2 - Infrared Spectrum of Ruthenocene (2-lb. sample)  
(KBr)

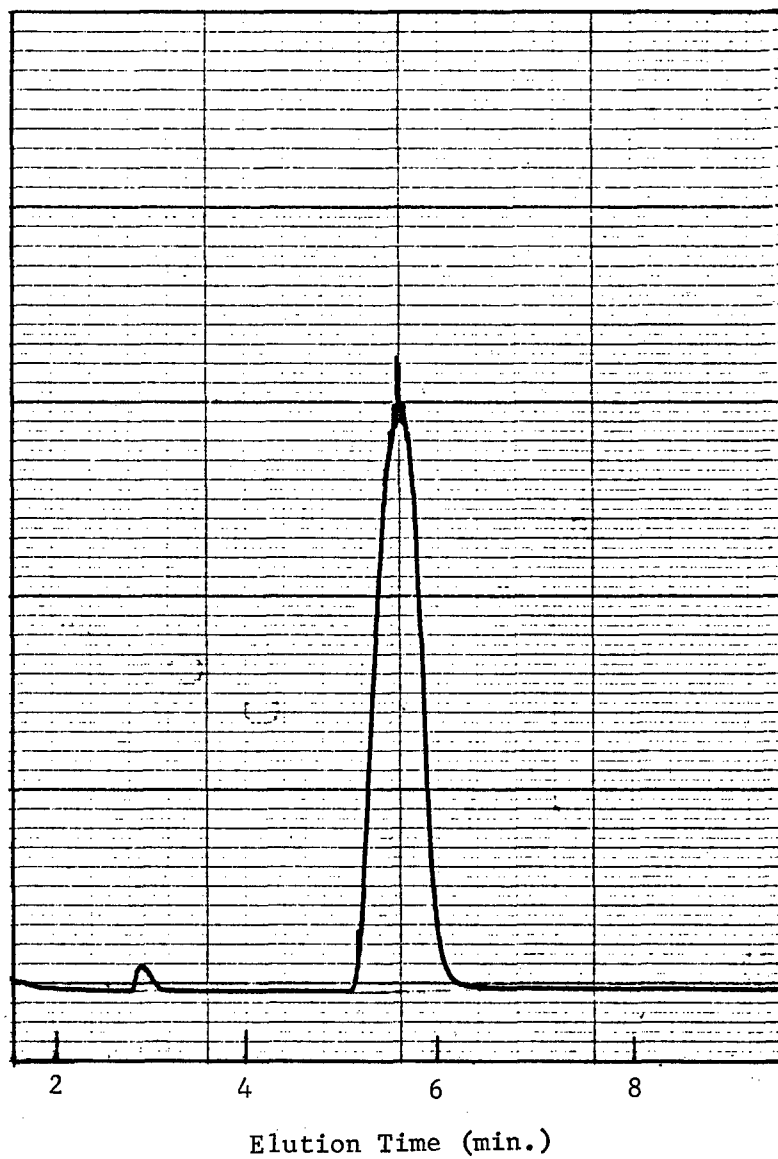


Figure 3 - Gas Liquid Chromatogram of Ruthenocene (2-lb. sample)  
(1-m. column, 5% SE 30 on Chromoport XXX, N carrier,  
60 ml/min, 117°)

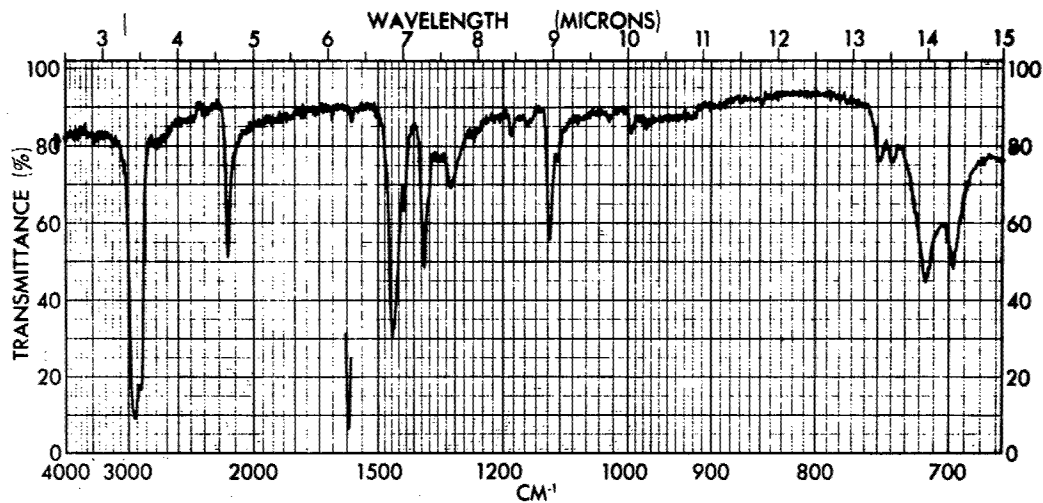


Figure 4 - Infrared Spectrum of Triphenylsilicon Azide  
(Sample No. 1) (Nujol)

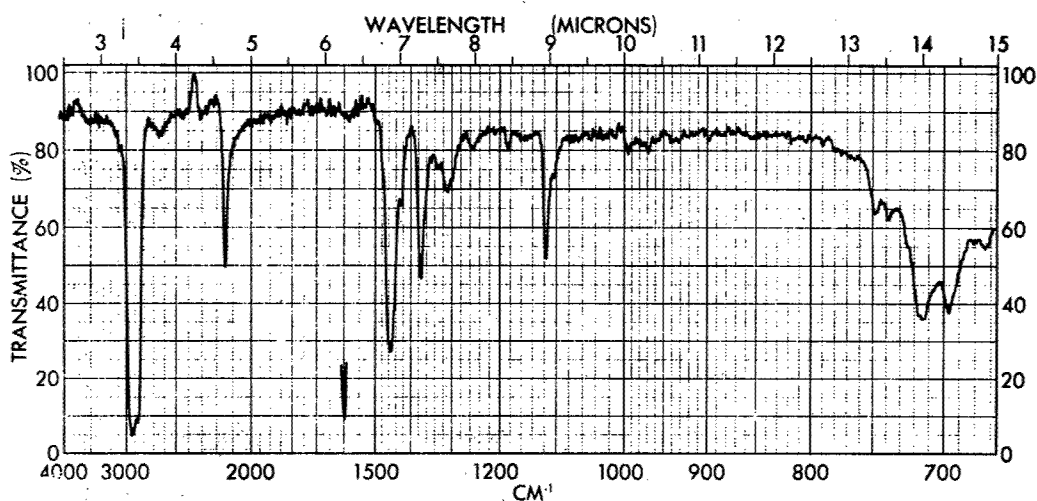


Figure 5 - Infrared Spectrum of Triphenylsilicon Azide  
(Sample No. 2) (Nujol)

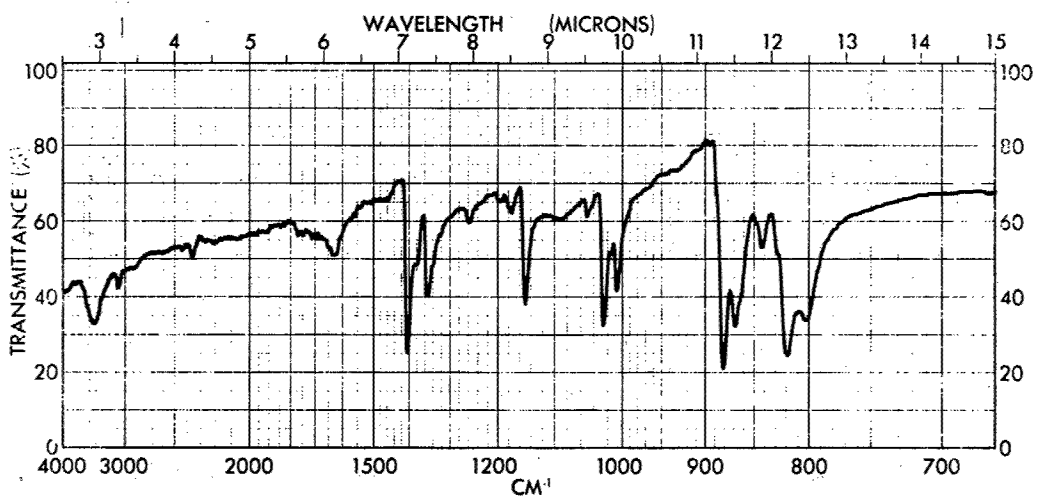


Figure 6 - Infrared Spectrum of 1,1'-Dibromoferrocene  
(KBr)

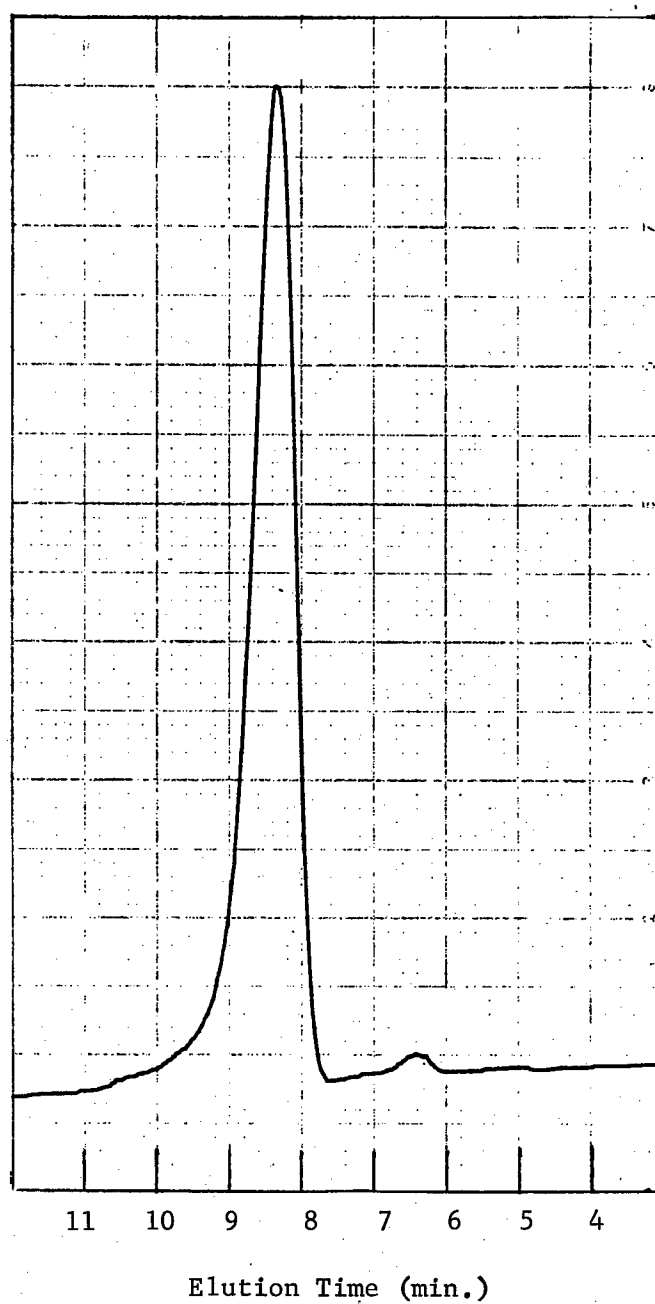


Figure 7 - Gas Liquid Chromatogram of 1,1'-Dibromoferrocene (2-m. column, 5% SF 96 on Gas Chrom Q, He carrier, 50 ml/min, 165°)

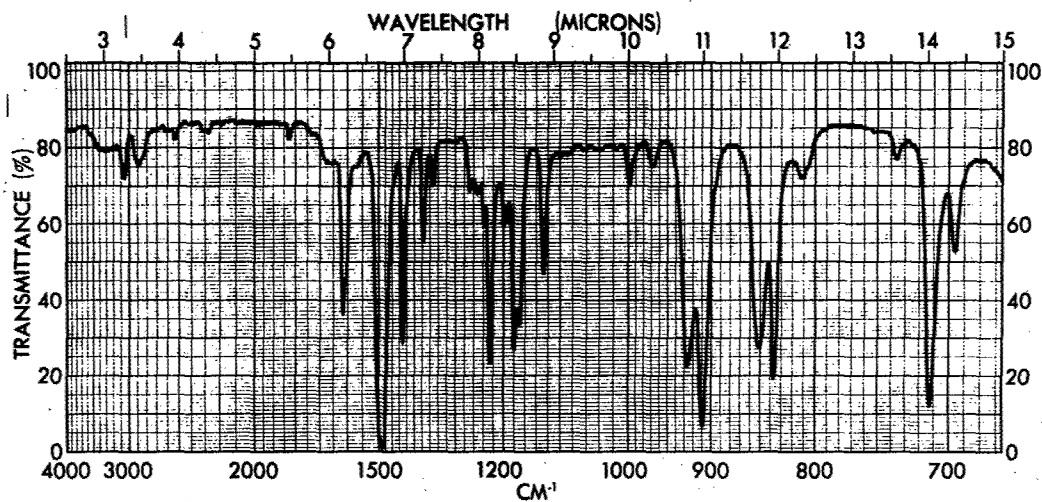


Figure 8 - Infrared Spectrum of 1-Iodo-2,3,5,6-tetrafluorobenzene (Liquid)

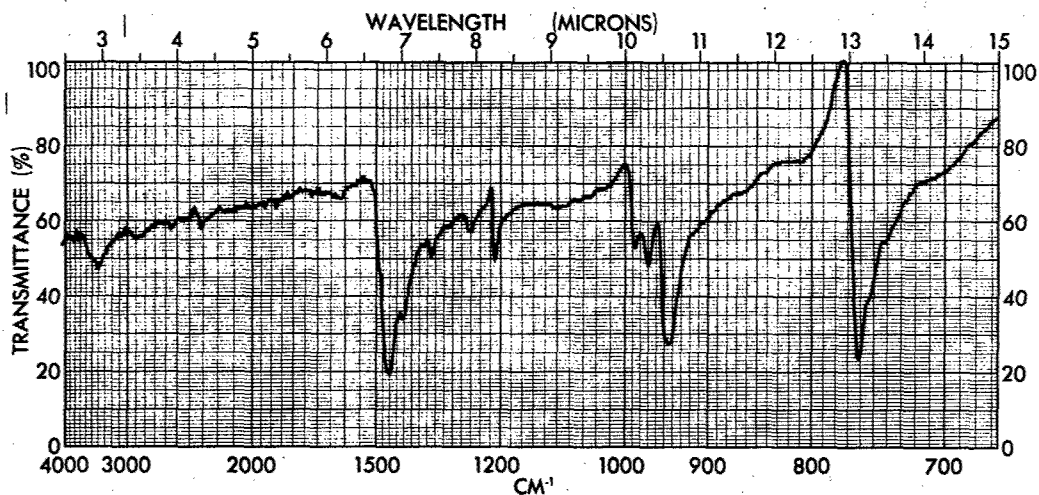


Figure 9 - Infrared Spectrum of 1,4-Diiodo-2,3,5,6-tetrafluorobenzene (KBr)

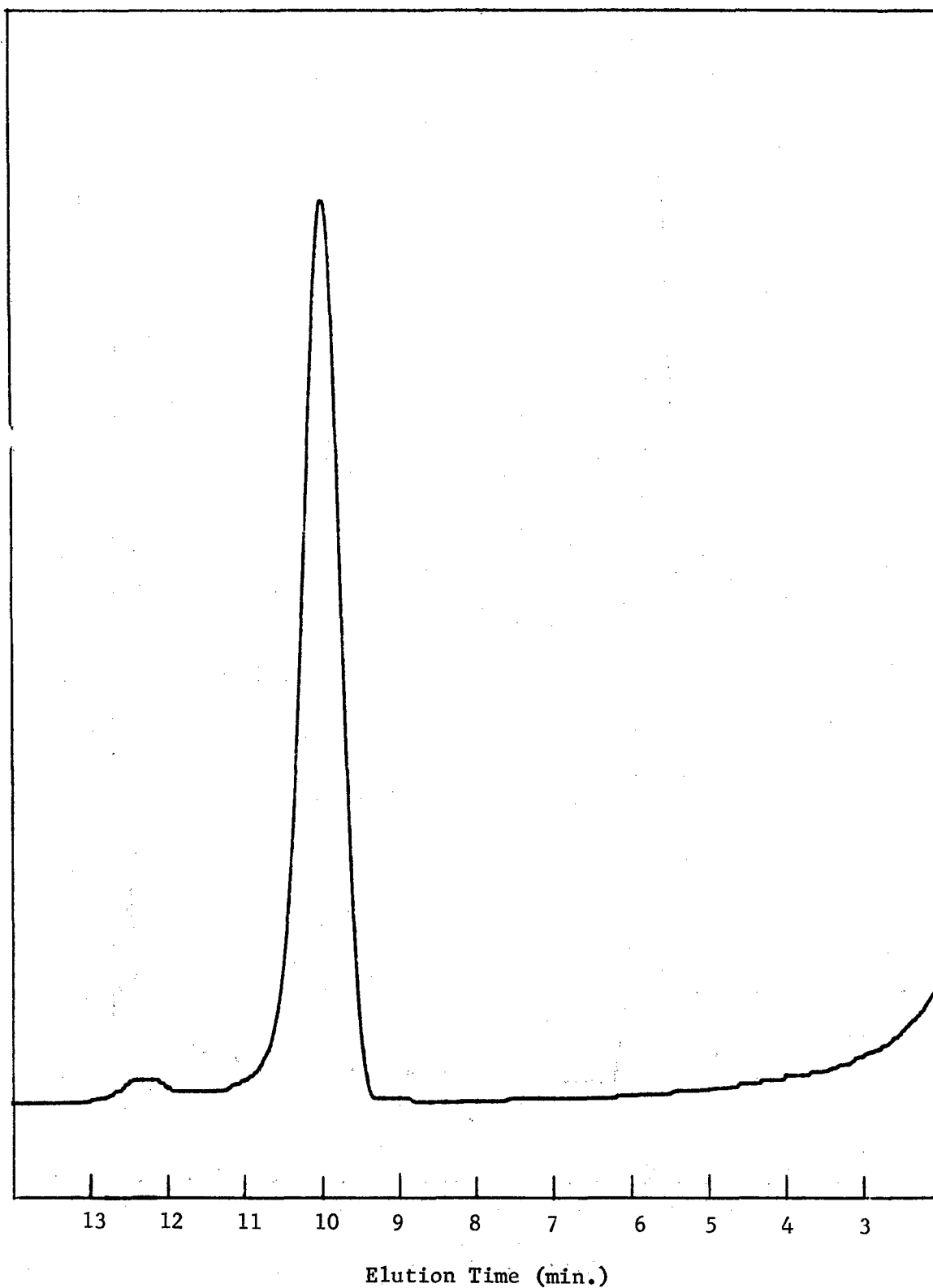


Figure 10 - Gas Liquid Chromatogram of 1-Iodo-2,3,5,6-tetrafluorobenzene  
(2-m. column, 20% SF 96 on Gas Chrom Q, He carrier, 45 ml/min, 124°)

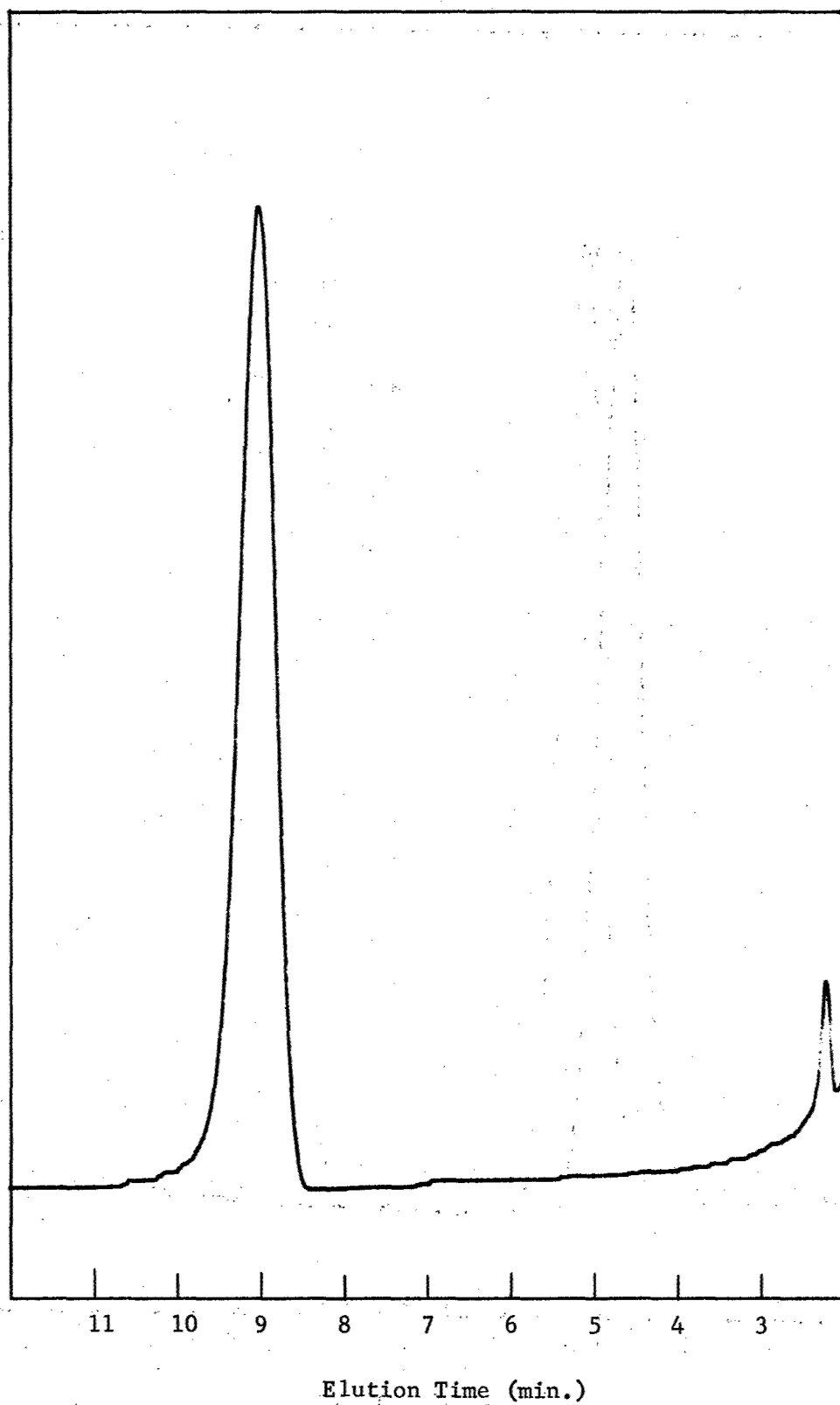


Figure 11 - Gas Liquid Chromatogram of 1,4-Diiodo-2,3,5,6-tetrafluorobenzene  
(2-m. column 20% SF 96 on Gas Chrom Q, He carrier, 40 ml/min, 181°)

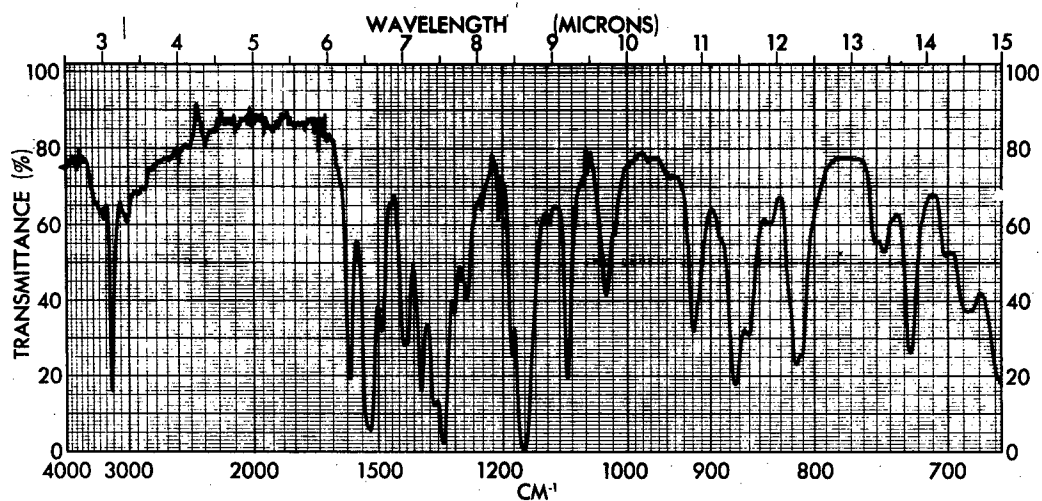


Figure 12- Infrared Spectrum of 4,5-Dinitro-N,N'-o-phenylenebis(p-toluenesulfonamide) (KBr)

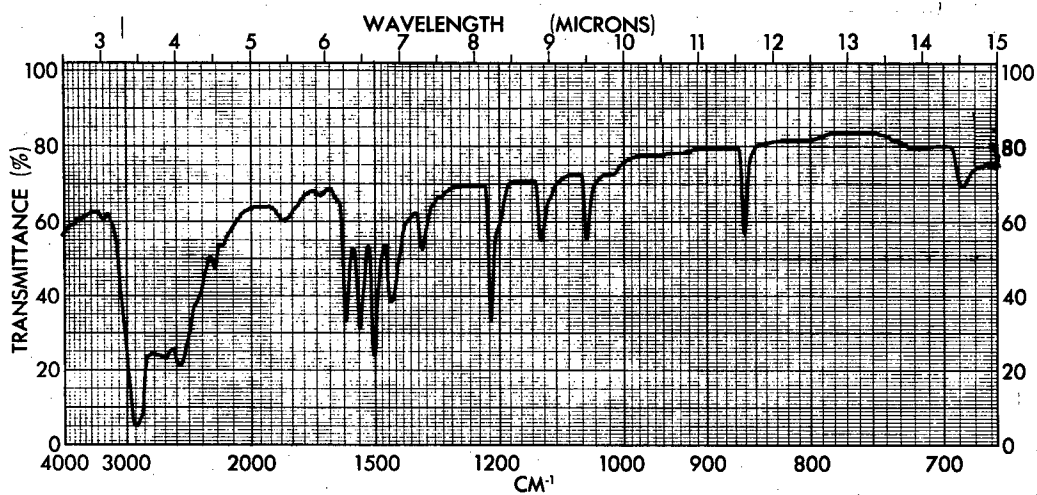


Figure 13 - Infrared Spectrum of 1,2,4,5-Tetraaminobenzene Tetrahydrochloride (Nujol)



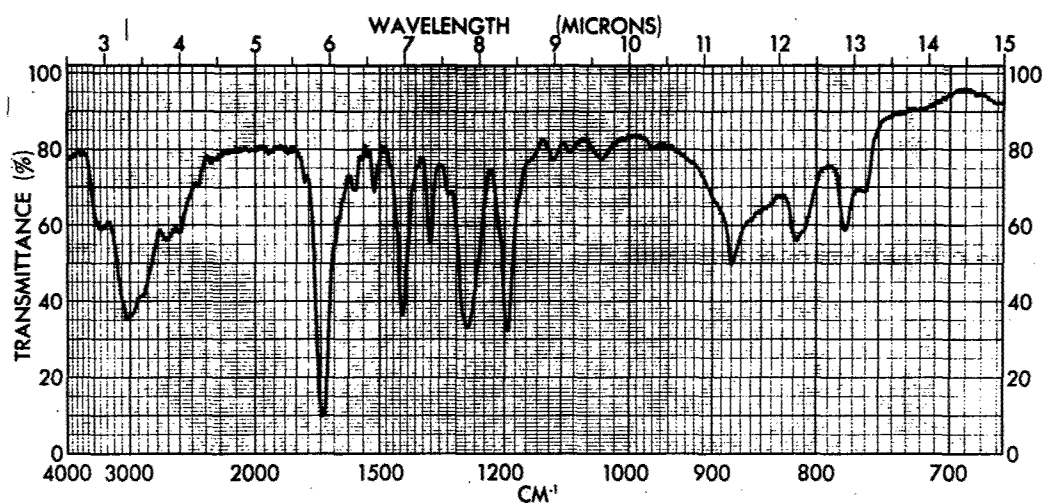


Figure 14 - Infrared Spectrum of 1,4,5,8-Naphthalene Tetracarboxylic Acid (KBr)

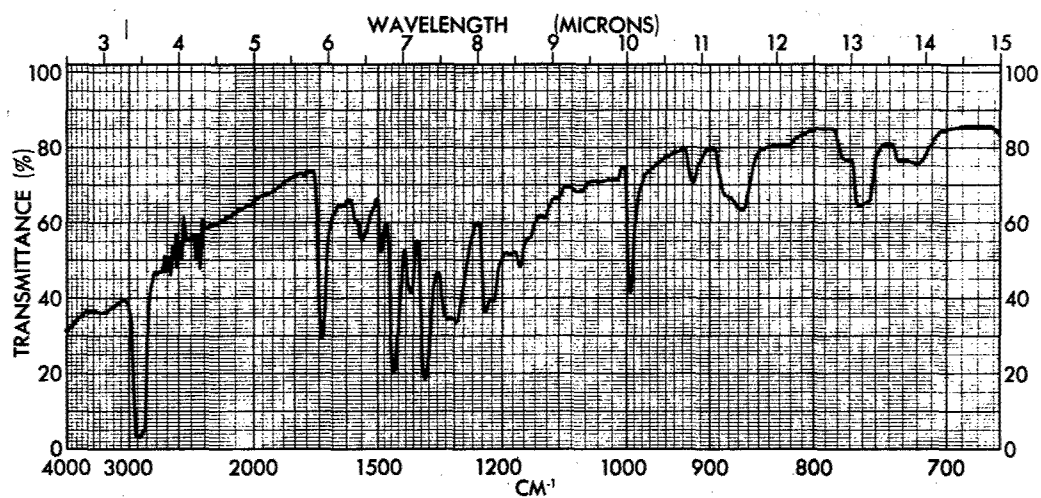


Figure 15 - Infrared Spectrum of the BBL Polymer (Nujol)

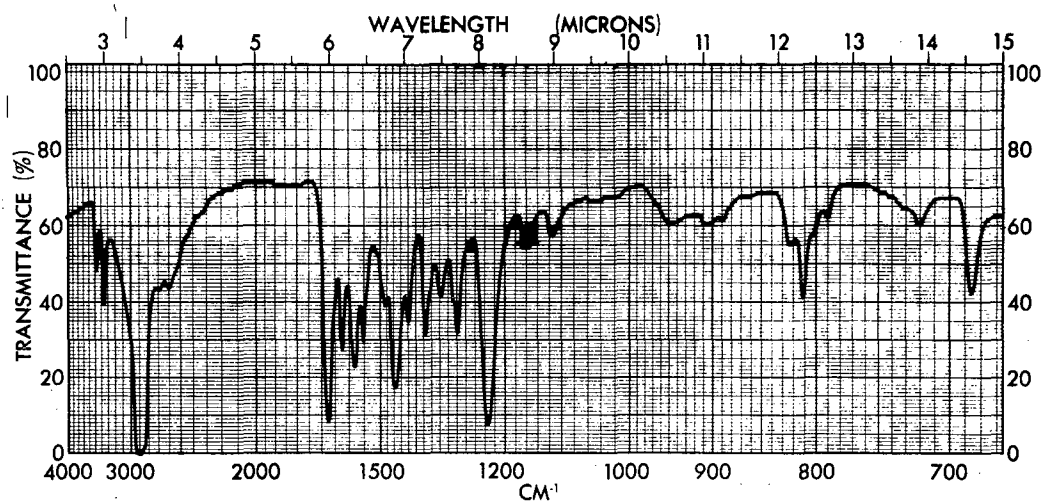


Figure 16 - Infrared Spectrum of Benzidine 3,3'-Dicarboxylic Acid (Sample No. 1) (Nujol)

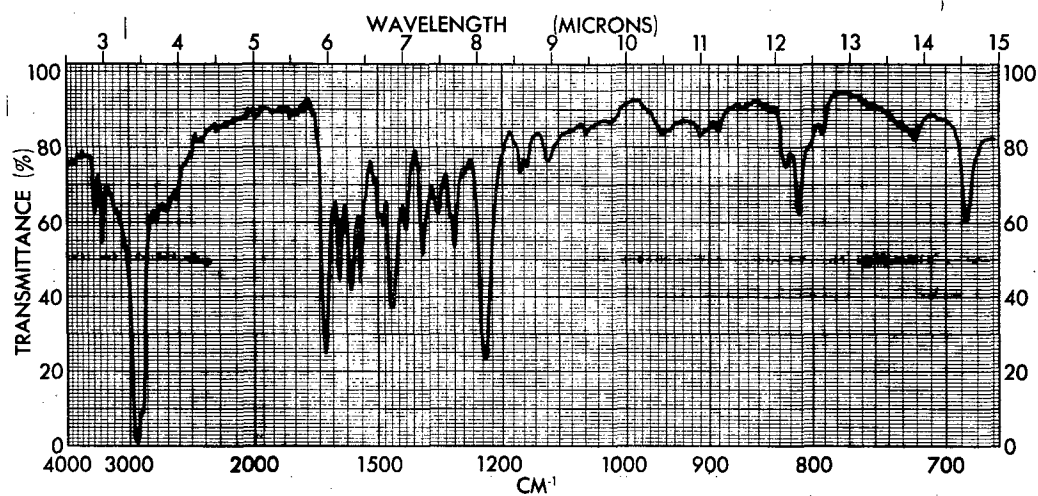


Figure 17 - Infrared Spectrum of Benzidine 3,3'-Dicarboxylic Acid (Sample No. 2) (Nujol)

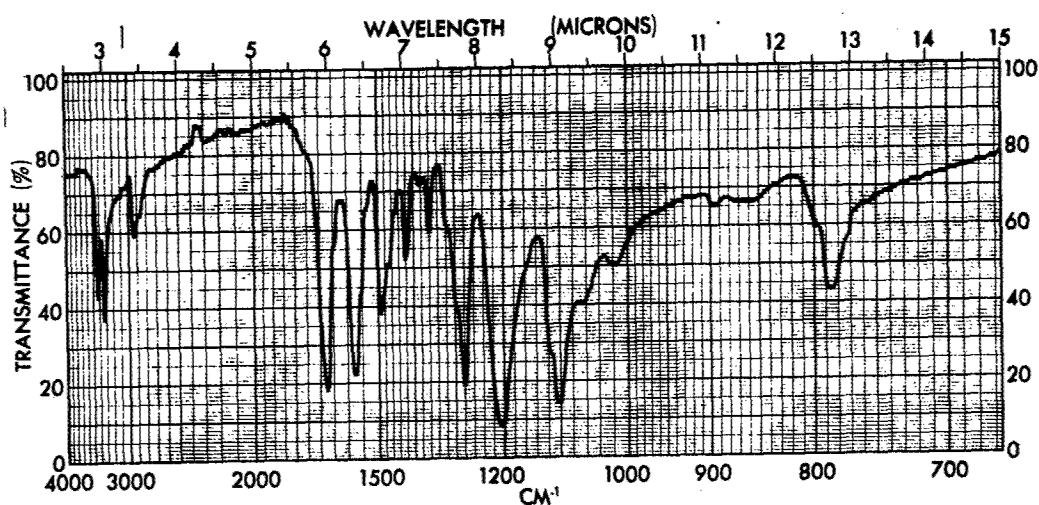


Figure 18 - Infrared Spectrum of Diethyl 2,5-Diaminoterephthate (KBr)

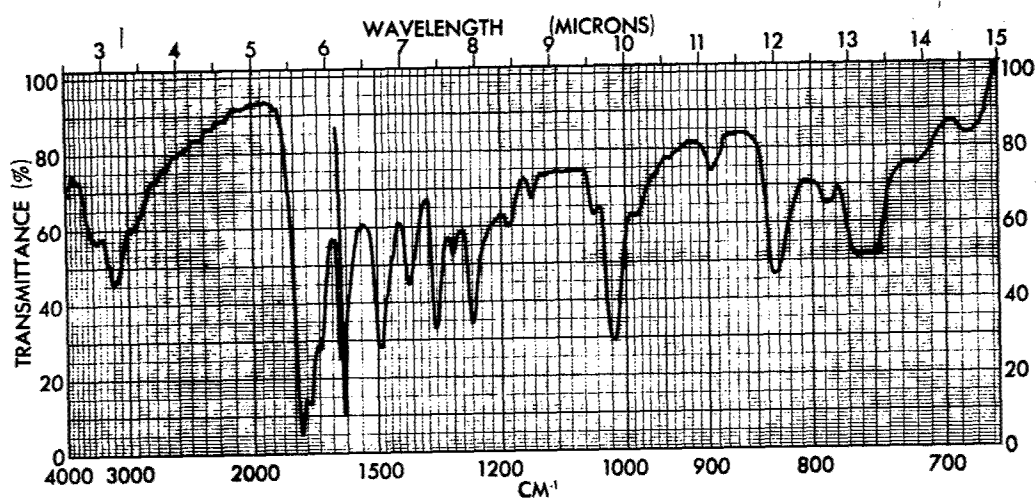


Figure 19 - Infrared Spectrum of 6,6'Bis([4H],3,1-benzoxazine-2,4-[1H]dione) (KBr)

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13. ABSTRACT Work on the synthesis of the following substances is reported: ruthenocene, 1,1'-diiodoferrocene, triphenylsilicon azide, 1,1'-dibromoferrocene, 1-iodo-2,3,5,6-tetrafluorobenzene, 1,4-diiodo-2,3,5,6-tetrafluorobenzene. 4,5-dinitro-N,N-o-phenylenebis(p-toluenesulfonamide), poly [(7-oxo-7H,10H-benze[de]imidazo-[4',5':5,6]benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL), benzidine 3,3'-dicarboxylic acid, diethyl 2,5-diaminoterephthalate, and 6,6'-bis-([4H],3,1-benzoxazine-2,4-[1H]dione).  (This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Polymer Branch, MANP, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.)			

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